What controls ozone production and loss in outflow from Asia: Observations of NO and NOy on the C-130 during ACE-Asia.

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Abstract

ACE-Asia is a major international program focused on the atmospheric chemistry and physics of aerosols coming off the Asian continent. ACE-Asia campaigns will begin during the spring of 2001 with an extensive network of ground, ship and aircraft observations.

Previously we have shown that anthropogenic pollutants form Asia can be transported to North America during spring in as little as 5-6 days. We have now observed pollutant transport events containing both high and low mixing ratios of ozone. To date, we do not understand what controls whether or not these polluted airmasses will contain elevated ozone. A number of hypotheses are presented which could explain the high and low ozone events based on initial NOx or NMHC mixing ratios, temperature, UV radiation fields, aerosol loading and/or aerosol reactivity. We propose to add measurements of NO and NOy to the suite of gas and aerosol measurements to be made on the NCAR C-130 aircraft during the first ACE-Asia campaign (spring of 2001) to examine these hypotheses. The measurements will be made with an existing high sensitivity instrument which has previously been flown successfully and demonstrated its ability to make high quality measurements. The NO and NOy data, along with other key chemical species measured on the C-130, will be used to address the question of what controls ozone production and loss in the outflow from Asia?

I. Results from NSF support:

<u>Photochemical Ozone Budget of the Eastern North Pacific Atmosphere (PHOBEA). National Science Foundation/Atmospheric Chemistry ATM-9529604 (U-Alaska) and ATM-9896270 (grant transferred to U-Washington), June 1996-June 2000, $473,000.</u>

In this project we made ground and airborne measurements of NOx, PAN, CO, NMHCs, O_3, and etc in the Northeastern Pacific region. The goals of this project are (1) to evaluate the role that PAN decomposition plays on photochemistry in this region during spring and (2) to quantify the impact that upstream Asian emissions has on the atmospheric chemistry in this region. Three measurement campaigns have been conducted:

Cheeka Peak Observatory, March-April, 1997 (NOx, PAN, CO, NMHCs, $J(NO_2)$, O_3, aerosol scatter, aerosol absorption, CPC and Rn)

Cheeka Peak Observatory, March-April, 1998 (same as 1997)

Kingair observations, March-April 1999, 14 flights under westerly conditions near the Washington coast. (NO, PAN, O_3, $J(NO_2)$), aerosol scatter, aerosol absorption, CPC, NMHCs and CO)

Publications to date:

Jaffe D.A., Anderson T., Covert D., Kotchenruther R., Trost B., Danielson J., Simpson W., Berntsen T., Karlsdottir S. Blake D., Harris J., Carmichael G. and Uno I. Transport of Asian Air Pollution to North America. *Geophys. Res. Letts.* 26, 711-714, 1999.

Anderson, T. L., Covert, D. S., Wheeler, J. D., Harris, J. M., Perry, K. D., Trost, B. E., Jaffe, D. J., and Ogren, J. A. Aerosol backscatter fraction and single scattering albedo: measured values and uncertainties at a coastal station in the Pacific NW, J. Geophys. Res. 104, 26,793-26,807, 1999.

Berntsen T.K., Karlsdottir S. and Jaffe D.A. (1999) Influence of Asian emissions on the composition of air reaching the Northwestern United States. *Geophys. Res. Letts.* 26, 2171-2174, 1999.

2 other papers are currently in preparation

A Study of the High Latitude Nitrogen Oxide Reservoir, NSF, ATM-9215127, 10/92-2/96, $373,800.

A total of three measurement campaigns were conducted during the three years of this project (listed below). In addition to the measurement campaigns we utilized a 0-d photochemical box model in collaboration with Sasha Madronich (NCAR) to evaluate the role of PAN decomposition on local photochemistry.

Measurement campaigns:

Poker Flat, AK, March-April 1993; PAN, O_3, NMHCs (Blake), and $RONO_2$'s (Atlas).

NyAlesund, Svalbard February-May, 1994: NOx, PAN, O_3, J(NO_2), NMHCs, aerosols and meteorology.

Poker Flat, Alaska, February-May, 1995; NO,NO_2, PAN, O_3, NMHCs, NOy, CO, CN and meteorology.

Publications:

Beine, H.J., M. Engardt, D.A. Jaffe, Ø, Hov, K. Holmen, and F. Stordal, Measurements of NOx and aerosol particles at the Ny Ålesund Zeppelin mountain station on Svalbard: Influence of regional and local pollution sources, Atm. Env. 7, 1067-1079, 1996.

Beine, H.J., D.A. Jaffe, D.R. Blake, E. Atlas, and J. Harris, Measurements of PAN, Alkyl nitrates, ozone and hydrocarbons during spring in Interior Alaska, J. Geophys. Res. 101, 12,613-12,619, 1996.

Jaffe, D.A., T.Berntsen, I.S.A. Isaksen, A Global 3D Chemical Transport Model; 2. Nitrogen Oxides and Non Methane Hydrocarbon Results. J. Geophys. Res. 102, 21,281-21,296, 1997.

Solberg S., T. Krognes, F. Stordal, O. Hov, H. J. Beine, D. A. Jaffe, K. C. Clemitshaw, S. A. Penkett. Reactive Nitrogen Compounds at Spitsbergen in the Norwegian Arctic. *J. Atm. Chem*. 28, 209-225, 1997

Beine, H.J., Daniel A. Jaffe, John A. Herring, Jennifer A. Kelley, Terje Krognes, Frode Stordal. High Latitude Springtime Photochemistry Part I: NOx, PAN and Ozone Relationships J. Atm. Chemistry 27, 127-153,1997.

Herring, John A., Daniel A. Jaffe, Harald J. Beine, Sasha Madronich, and Donald. R. Blake. High-Latitude Springtime Photochemistry Part II: Sensitivity Studies of Ozone Production J. Atm. Chemistry 27, 155-178,1997.

Beine H., Jaffe D.A., Stordal F., Engardt M., Solberg S., Schmidbauer N. and Holmén K. NOx during ozone depletion events in the Arctic troposphere at Ny-Ålesund, Svalbard. Tellus 49, 556 - 565, 1997.

<u>Ground Based Measurements of Nitrogen Oxides as Part of the Pacific Exploratory Mission-West Program, NSF, ATM-9022004, 1/91-12/93, $99,000.</u>

In this project we first participated in an informal intercomparison for NO and NOy measurements in ambient air with the NOAA Aeronomy Lab. We then conducted measurements of NO, NOy, CO and O_3 in collaboration with Dr. Hajime Akimoto at Oki Island, Japan. From the measured mixing ratios we were able to estimate O_3 production rates for the Oki Island site which were reasonably consistent with the aircraft data taken in the 0-1 km “continental airmasses”.

Measurement campaigns:

Intercomparison of NO and NOy techniques with NOAA-Aeronomy Lab- Green Mesa Boulder, Colorado. February 1991.

Oki Island, Japan, Sept-Oct. 1991

Publications:

Jaffe D., Parrish D., and Goldan P. Report on Boulder NO/NOy Intercomparison, Report to the NSF, May 1991.

Jaffe, D.A., R.E. Honrath, L. Zhang, H. Akimoto, A. Shimizu, H. Mukai, K. Murano, S. Hatakeyama and J. Merill, Measurements of NO, NOy, CO and O_3 and estimation of the ozone production rate at Oki Island, Japan during PEM-West. J. Geoph. Res. 101, 2037-2048, 1996.

Akimoto H., Mukai H., Masataka N., Liu C.M., Buhr M., Hsu K.T., Jaffe D.A., Zhang L., Honrath R., Merrill J.T., and Newell R.E., Long Range Transport of Ozone in the East Asian Pacific Rim Region, J. Geophys. Res. 101, 1999-2010, 1996.

<u>Tropospheric Nitrogen Oxide Chemistry in Central Alaska, NSF, ATM-8814518, 9/88-3/92, $299,202.</u>

During this project instrumentation for measurements of NO and NOy were built, tested and deployed. Three field campaigns were made at Barrow, Alaska (no suitable site in central Alaska was available at that time).

Measurement campaigns at Barrow:

July-Aug. 1988

March-April 1989

Feb.-Oct. 1990

The results indicated a substantial seasonal cycle of NOy, with highest values in the spring. We also identified an influence from synoptic systems, with higher NOy in arctic airmasses, as compared to pacific marine air masses arriving at Barrow. During late spring a pulse of NO is observed, consistent with an important role for PAN decomposition. A strong correlation of NOy with O_3 during summer is observed, probably due to boundary layer exchange.

Publications:

Honrath, R.E. and D.A. Jaffe, Measurements of nitrogen oxides in the Arctic, Geophys. Res. Letts., 17, 611-614, 1990.

Honrath, R.E., Nitrogen oxides in the Arctic troposphere. Ph.D Thesis, University of Alaska Fairbanks, Fairbanks, Alaska. September 1991.

Jaffe, D.A., R.E. Honrath, J.A. Herring, S.M. Li, and J.D. Kahl, Measurements of nitrogen oxides at Barrow, Alaska during spring: Evidence for regional and Northern Hemispheric sources of pollution, J. Geophys. Res., 96, 7395-7405, 1991.

Honrath, R.E. and D.A. Jaffe, The seasonal cycle of nitrogen oxides in the Arctic troposphere at Barrow, Alaska, J. Geophys. Res., 97, 20,615-20, 630, 1992.

Jaffe, D.A. and M.D. Zukowski, Nitrate deposition to the Alaskan snowpack, Atmos. Environ., 27A, 2935-2941, 1993.

Jaffe, D.A., Relationship Between Anthropogenic Nitrogen Oxides and Ozone Trends in the Arctic Troposphere, In: eds H. Niki and K.H. Becker, The Troposphere Chemistry of Ozone in the Polar Regions. NATO ASI Series, Springer-Verlag, N.Y., 1993.

Jaffe, D.A., R.E. Honrath, D. Furness, T.J. Conway, E. Dlugokencky, and L.P. Steele, An estimate of the CH4, NOx, and CO_2 emissions from the Prudhoe Bay, Alaska, oil development, In press, J. Atmos. Chem. 20, 213-227, 1995.

II. Introduction

The East Asian region is one of the largest and most rapidly developing regions on the planet (e.g. Galloway et al., 1995; Elliot et al., 1997; Streets et al., 1999). From the mid-1970s to the 1990's the emissions of both NOx and SO_2 from the East Asian region increased at an average rate of ~4%/year and now exceed the emissions from other developed regions such as North America and Europe (Akimoto and Narita 1994; VanAardeen et al., 1999). Since the wind pattern in this part of the world is generally characterized by westerly flow, it is not surprising that transport of these pollutants into the central North Pacific has been clearly identified (Prospero and Savoie, 1989; Talbot et al., 1997; Jaffe et al., 1997).

The ACE-Asia project was developed to help reduce the uncertainties associated from both direct and in-direct climate forcing by anthropogenic aerosols in the East Asian region. This is particularly relevant to past and future climate change given the rapid increases in emissions which are now taking place in this region. The specific goals for this project are (ACE-Asia, 1999):

Objective 1. Determine the physical, chemical, and radiative properties of the major aerosol types in the Eastern Asia and Northwest Pacific region and investigate the relationships among these properties.

Objective 2. Quantify the physical and chemical processes controlling the evolution of the major aerosol types and in particular their physical, chemical, and radiative properties.

Objective 3. Develop procedures to extrapolate aerosol properties and processes from local to regional and global scales, and assess the regional direct and indirect radiative forcing by aerosols in the Eastern Asia and Northwest Pacific region.

We have recently shown that Asian combustion products can be transported to the west coast of the U.S., when the meteorological conditions are favorable [Jaffe et al., 1999]. These were identified based on measurements of CO, peroxyacetyl nitrate (PAN), Radon, aerosols, and volatile organic carbon compounds (VOCs) at the Cheeka Peak Observatory (CPO) on the western tip of Washington state (48.3^{o}N 124.6^{o}W, 480m), combined with isentropic back-trajectories. While several occurrences were identified in our spring 1997 observations, the most prominent took place on March 29th, 1997. However what is notable about this event is the fact that ozone was not enhanced, despite the presence of both elevated PAN and NMHCs.

During 1999 observations of a number of chemical species were made from a small aircraft, the Wyoming Kingair (twin engine turboprop) off the coast of Washington state for 6 weeks (March 20, 1999-April 28, 1999). The aircraft was equipped with instrumentation for measurements of NO, O_3, PAN, CO, VOCs, J(NO_2), aerosol scatter and aerosol absorption. Of the 14 research flights made, all taken during periods of strong westerly flow, five of these encountered layers with significantly enhanced aerosol and gaseous pollutant concentrations. The data on April 9th, 1999 showed layers between 3-6 km containing substantially elevated mixing ratios of PAN, CO, NMHCs, O_3, aerosol scatter and absorption. The O_3 mixing ratio in these layers reached a maximum of 85 ppbv, and the fact that aerosols, PAN and NMHCs were elevated simultaneously demonstrates that this O_3 was not of stratospheric origin, but was mostly likely from tropospheric photochemistry. Isentropic trajectories for these layers showed transport from the region near southern Japan/Korea/China.

While we have other examples of long range transport, it is useful to explore these two cases in some detail to attempt to understand why some long range transport events contain elevated O_3 while others do not. Based on isentropic back trajectories (calculated by Joyce Harris, NOAA-CMDL) the airmass sample <u>at the surface</u> on 3/29/97 crossed over northern Japan, northeastern China and the southeastern portion of Russia, whereas the airmass sampled at 5 km on 4/9/99 crossed over southern Japan, Korea and eastern China. Thus, the trajectory for the 4/9/99 event crosses over regions with higher population and emission densities. While it is tempting to conclude that the O_3 difference is due solely to this source region difference, two facts make it difficult to do this:

1) Isentropic trajectories have a number inherent assumptions and sources of errors which limits their accuracy (e.g. Kahl, 1996). For example Stohl (1998) suggests that a typical trajectory uncertainty is about 20% of the distance traveled. Thus it is not appropriate to use the trajectory to discriminate between two source regions which are

separated by a similar distance as the trajectory uncertainty;2) These two different events have rather similar aerosol and NMHC levels, suggesting, that the original source regions were somewhat similar. On the other hand PAN mixing ratios are about a factor of two higher in the 4/9/99 event (400 vs. 200 pptv).

There are two other important differences between the 3/29/97 and 4/9/99 events. Examining temperature trends over the Asian source regions for the times when the trajectories indicate the air mass originated over these regions (approximately 6 days prior to arrival in both cases) shows that temperatures at the surface in the Asian source regions for the 4/9/99 event was about 7-10^{o}C warmer (24 hour average), as compared to the 3/29/97 event. A second difference is that the 3/29/97 event arrived at CPO with a substantial amount of seasalt aerosol, based on Na and Cl measurements by PIXE. This was due to the fact that the airmass had been traveling for several days in the marine boundary layer with high wind speeds (Jaffe et al., 1999). The presence of this high seasalt aerosol suggests that halogen/HOx reactions could have diminished the amount of O_3 that might have been present initially (e.g. Finlayson-Pitts et al., 1990).

While mineral aerosol can also result in reduced O_3 mixing ratios due to chemical reactions (e.g. Zhang and Carmichael, 1999), the PIXE aerosol data from the 3/29/97 event indicates that mineral aerosol concentrations were low at this time. So while this mineral aerosol may be important to O_3 chemistry, we do not believe it explains the lack of an O_3 enhancement observed on 3/29/99.

A number of projects have investigated ozone production and export in highly impacted regions. This includes the NARE investigations (Fehsenfeld et al., 1996; Penkett et al., 1998), the PEM-West studies (Hoell et al., 1997), and the SOS investigation (Meagher et al., 1998). While there is insufficient space in this proposal to explore these in depth, I will summarize some of the most pertinent results from these major studies.

The PEM-West program examined O_3 and precursor gases in the western Pacific during both fall (PEM-West A) and spring (PEM-West B) seasons. Generally mixing ratios for many species was considerably higher during spring due to both a seasonal cycle and enhanced outflow from the Asian continent (Talbot et al., 1997). However, while this region was characterized by generally positive net O_3 production, the median production rates in the PEM-West study area at all altitudes were generally not large (less than 1 ppbv/day) as a result of the low NO mixing ratios (Crawford et al., 1997). This is a result of the fact that the PEM-West study area generally sampled air which had been transported for 1 or more days from the Asian continent. Given the short lifetime for NOx, it is not surprising that only modest *in-situ* O_3 production rates were found. However, it is also somewhat surprising that median ozone mixing ratios were not higher than they were, given the elevated mixing ratios of other anthropogenic tracers. For example mean CO, NOy, ethane and propane mixing ratios in outflow from Asia were 206 ppbv, 1.1 ppbv, 2337 pptv and 961 pptv in the 0-2 km region, all significantly enhanced over background values, whereas the mean O_3 mixing ratio was barely enhance at 44 ppbv (Talbot et a., 1997). This likely reflects the lower O_3 production efficiency during the late-winter early spring season.

Similarly, the NARE campaigns have examined ozone production and outflow from the North American continent. Duderstadt et al. (1998) calculated net O_3 production for Sable Island, Nova Scotia to obtain positive production rates of 3.6, ppbv/day, comparable to the production rates we obtained at Oki Island, Japan during PEM-West A (Jaffe et al., 1996), but larger than the rates observed from the PEM-West B aircraft data mentioned above. This is consistent with higher production rates during summer/early fall seasons and at surface sites which are closer to emission source regions. In addition, Parrish et al (1993; 1998) have shown good correlations of CO and O_3 during summer at a number of sites downwind of U.S. emissions.

Finally, from the SOS studies (Meagher et al., 1998) a number of important parameters have been investigated including the role of biogenic hydrocarbons, the NOx/NMHC ratios and the significance of the high temperatures and UV fields observed in the SOS study region during summer. In general, a number of papers have pointed to the very high levels of OH in the SOS study region during summer, resulting in rapid oxidation of many NMHCs and a lifetime for NOx of less than 0.5 days (e.g. Nunnermacker et al., 1998).

A number of models have been used to integrate and understand the production and export of O_3 from continental regions. For example Jacob et al. (1993) have used a regional model to examine the parameters controlling ozone production and export. They find that as a result of the short NOx lifetime, only about 6% of the NOx that is emitted in the U.S. gets exported from the boundary layer, whereas about 70% of the O_3 that's produced gets exported. In addition the Harvard model has shown (Chin et al., 1994) that using the observed CO-O_3 correlation alone will significantly underestimate the total O_3 production.

Based all of the evidence above, it is reasonable to conclude that most of the O_3 enhancement that we observed being transported to North America during the 4/9/99 event results from O_3 production in the polluted east Asian boundary layer. Thus, while some O_3 production can still occur outside of the high emission region (Crawford et al., 1997) we believe that this cannot explain the high mixing ratios we observe on 4/9/99, which arrived concurrently with high CO, NMHCs, PAN and aerosols.

Thus, the basic question we would like to explore in this project is "What controls O_3 production and loss during outflow of polluted airmasses from Asia?" There are a number of possible answers to this question on both the production and loss side of the equation:

1) Low production due to source region emissions of NOx and NMHCs (e.g. Sillman, 1999);
2) Low source region temperature (Silman and Samson, 1995; Jacob et al., 1993);
3) Low source region radiation fields due to clouds and/or aerosol loading (Dickerson et al., 1997; Jacobson, 1998; He et al., 1999; Liao et al., 1999);
4) O_3 losses due to interaction with seasalt aerosols;
5) O_3/NOx/HOx losses due to interaction with mineral aerosols (e.g. Mozurkewich and Calvert, 1988; Dentner and Crutzen, 1993; Denter et al., 1996; He and Carmichael, 1999)

or some combination of these factors.

So the primary objectives of this work are:

1) Make measurements of NO and NOy onboard the NCAR C-130 aircraft during the spring 2001 campaign.

2) Calculate NO_2 mixing ratios from a photochemical model and the C-130 observations;
3) Use the NO and NOy observations and model calculated $NO_{2,}$ along with other data collected onboard to examine ozone mixing ratios as a function of many different parameters (e.g. O_3 relationship to CO, NOy, NO_Z, source emission characteristics, source temperature and radiation characteristics, aerosol loading and aerosol chemistry)
4) Use a standard NOx/HOx/ROx 0-D photochemical model to calculate OH concentrations and O_3 production rates based on measured NO and other observed parameters, similar to the method used by Davis et al. (1996) and our previous work (Herring et al., 1997).

While we recognize that O_3 photochemistry is not the highest priority within ACE-Asia, our measurements will make an important contribution to the overall project goals. This is because oxidative processes are central to the ACE-Asia objectives. For example, quantifying the production of non-seasalt sulfate aerosols from SO_2 will require knowledge of the O_3 and OH concentrations. Because direct measurements of OH will not be made on the C-130, OH fields will need to be calculated from a photochemical model, and for this, NO mixing ratios are essential. Similarly a number of modeling groups will use the ACE-Asia data to examine the production and loss of a variety of gaseous and aerosol species. NO and NOy observations will significantly add to the value of these modeling results. In addition these observations represent a significant "value-added" component to the C-130 platform, utilizing space on an expensive platform that would otherwise be unfilled.

Experimental procedures

A single, high sensitivity chemiluminescence instrument will be used for both NO and NOy measurements.

NO

NO will be measured using a high sensitivity chemiluminescence detector similar in design to other high sensitivity instruments (Kley and McFarland, 1980; Drummond et al., 1985; Ridley et al., 1988). The instrument to be used was designed and built by the PI and coworkers specifically for aircraft work and was used successfully during the 1999 "PHOBEA" aircraft campaign. It exhibits high sensitivity, a fast response time, and a rapid "power-on" to measurement time. At the heart of the instrument is the reaction chamber, which is based on the design of Ridley and Grahek (1990) with minor modifications. In the reaction chamber the NO+O_3 reaction and the resulting photons are detected by a dry ice cooled, red sensitive photomultiplier tube (Hamamutsu R-1333). The instrument also uses water addition (Ridley and Grahek, 1990) to minimize the effect of rapid changes in humidity on the zero level.

The instrument consists of four main units. (1) The main NO box contains the reaction chamber, PMT, PMT cooler, mass flow controllers, solenoids, zeroing system, and signal electronics. A separate unit (2) contains the ozone generator, which generates ozone from a mass flow controlled supply of O_2 passed through high voltage discharge corona. (3) A two stage 28 volt D.C. vacuum pump is connected to the reaction chamber via bellows tubing and the signal is read and processed via a (4) laptop computer. Pressurized cylinders of O_2 and NO calibration standard are also required. Table 1 lists the weight, dimensions, and power requirements of the four main components.

NO is measured by switching between four modes of operation: measure, zero, calibration, and calibration zero. Ambient air is sampled at a mass flow controlled rate of 1 slpm. The sample is then passed over a water vapor addition system, which mitigates the effects of ambient humidity fluctuations. The humidified sample stream passes through a zeroing volume, enters the reaction chamber, and mixes with ~4% O_3 in O_2 from the ozone generator. The reaction chamber is temperature controlled at 30°C. The sample stream exits the reaction chamber through a 1" ID stainless steel bellows tube connected to the vacuum pump equipped with a reactive gas trap filled with a catalyst for ozone removal.

The signal from the PMT is amplified by a photomultiplier amplifier discriminator, converted to a TTL signal, and read by a PCM-DAS16D/16 data acquisition card installed on a laptop computer. While this system was adequate on the Kingair, there were some problems with spurious noise from the aircraft electrical system. While this was generally fairly minor, we intend to improve this with a better pulse counting system prior to ACE-Asia. The photon count rate gets recorded both on the laptop and by the aircraft data system. The signal is zeroed in "zero" and "calibration zero" modes by diverting roughly 5% of the flow from the ozone generator into the sample stream just prior to the zeroing volume, with the remaining 95% of the ozone flow continuing to the reaction chamber. In flight calibrations are performed using standard addition of a NIST traceable NO calibration standard.

Instrument performance:

In the spring of 1999 this instrument was flown on 14 flights of the University of Wyoming's King Air research aircraft as part of the PHOBEA (Photochemical Ozone Budget of the Eastern North Pacific Atmosphere) experiment. The King Air was based in Everett, Washington during this time and we flew out over the North Pacific under conditions with strong westerly flow. As such, we typically measured NO mixing ratios of between 0-20 pptv. The instrument performed very well during this campaign and we gained a much better understanding of the instrument's performance and capabilities.

- *Warm-up time:* Between flights the instrument could not be run continuously, hence, it was necessary to restart the instrument before each flight. An instrument warm-up time of 3 hours was sufficient for zero mode signal stabilization.
- *Sensitivity to NO:* After the three hour warm-up period the instrument sensitivity typically ranged from 3.5 to 4.5 cps/pptv NO for a 5 hour flight. It generally increased as the instrument continued to "warm up" during the flight. This was monitored carefully with frequent in-flight calibrations.
- *Detection Limit:* The in-flight detection limit of this instrument was on average 2 pptv NO for a 9 minute signal integration time and 4 pptv for a 1 minute signal integration time.
- *Quality control measures:* The instrument showed no variations with ambient pressure. However, the instrument signal required some post flight corrections for switching response time constants, humidity fluctuations, and NO loss in the sample lines due to reaction with ambient ozone. Ambient humidity changes, while

mitigated by the use of a water vapor addition system, still had a small effect on the instrument's zero mode signal and sensitivity. This effect was characterized in our laboratory at the University of Washington. Corrections to the NO data due to humidity fluctuations were small, generally less than 1%. The other corrections were on the order of 5% or less in total. Extensive leak testing of the instrument and sample lines revealed no detectable cabin air leaks into the instrument. The instrument signal in zero mode was found to increase as a function of altitude due to the effects of cosmic rays on the PMT. The increase in zero mode signal was typically 10% from sea level to 8 km.

- *Signal Artifacts:* Determining the presence of signal artifacts is critical for the measurement of NO when the mixing ratio is low (Drummond et al., 1985). There are two standard methods to monitor instrument artifacts. Since NO is quickly converted to NO_2 by ambient ozone in the absence of light, the most reliable method is to measure NO at night in a region remote from sources of NO. Any significant deviation from zero likely reflects instrumental artifacts. A less reliable method is to measure the NO concentration in cylinders of high quality synthetic zero air. Zero air cylinders, however, may contain concentrations of up to a few pptv NO, thus making these tests somewhat less conclusive. Artifact tests were made during PHOBEA with zero air before every flight and during one 4-hour night flight. From 63 one minute averages during the night flight, the mean NO mixing ratio was -0.1 $\pm$ 1.6 pptv (mean $\pm$ 1 standard deviation). The time series of one minute averages from the night flight are depicted in Figure 1. Zero air measurements had more variability than the night flight measurements, but also centered around 0 pptv NO. From sixteen measurements made throughout the aircraft campaign, the mean NO concentration in zero air was -0.3 $\pm$ 2.9 (mean $\pm$ 1 standard deviation). Based on these tests, the NO instrument was considered free of artifacts during the PHOBEA experiment.

Measurement cycle:

During PHOBEA we were working in an environment where we expected to see NO mixing ratios of 20 pptv or less, but only relatively modest horizontal variations. As such, the measurement cycle we used was 20 minutes long; with 6 minutes for zeroing, 9 minutes for measurement, and 5 minutes for calibration. Because of this strategy, not only were we able to reliably detect low mixing ratios of NO in the remote North Pacific, but we also gained a much better characterization of our instrument's behavior.

Given the good instrument stability (both zero and sensitivity) and the much higher mixing ratios we expect in the ACE-Asia study region, we should be able to achieve a much shorter instrument cycle. Thus, we should be able to switch between NO and NOy measurements at least every 4 minutes and to do zero and calibrations once per half hour or hour. While we recognize that switching between NO and NOy modes on the C-130 platform is not ideal, the science objectives that we propose require measurements of both species. Adding a second channel to our existing one channel instrument would significantly add to the cost and complexity of this project The final measurement cycle will be worked out in collaboration with the ACE-Asia C-130 science team.

Table 1. NO Instrument weight, dimensions and power requirements.

Component	Weight (lbs)	Dimensions (in) (l x w x h)	power requirements
main NO box	65	24x17x14	120 VAC 2 A
ozone generator	25	13x17x7	120 VAC 2 A
vacuum pump	75	30x10x23	28 VDC 30 A (start-up) 20 A (continuous)
laptop computer	10	12x16x14 (when in use)	120 VAC 1 A
NOy converter (estimate)	10	4" diam. x 8"	120 VAC 2 A
Oxygen cylinder	20	7.25" diam. x 28 1/2" tall	None
NO in N_2 cylinder	15	6.75" diam. x 21" tall	None
Zero Air cylinder	20	7.25" diam. x 28 1/2" tall	None

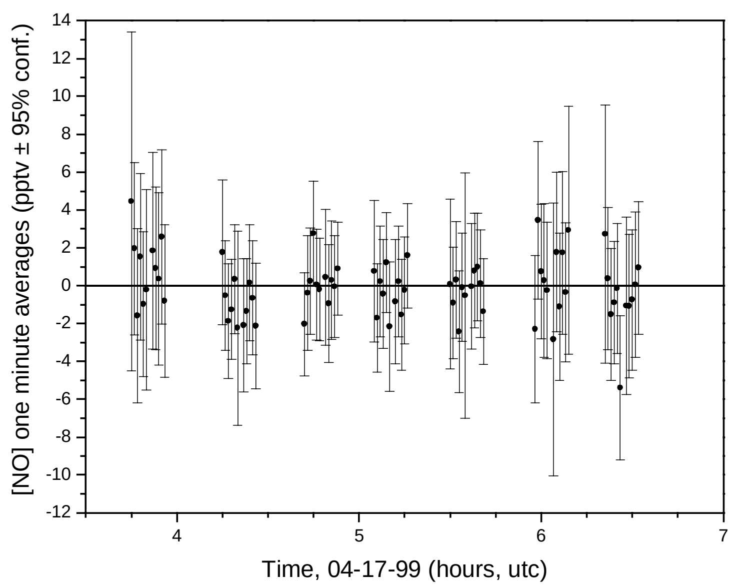

Figure 1. Mixing ratio (pptv) of NO during the PHOBEA night flight. Because of the reaction of O_3 with NO, we expect a value of zero.

NOy

NOy ($NOx+HNO_3+PAN+RONO_2$) will be measured using a heated surface converter. Previously, we have used a gold tube converter with 0.3% v/v CO added as the reducing agent (Fahey et al., 1985; Honrath and Jaffe, 1992). However, for the much higher mixing ratios expected in the ACE-Asia study region, and as a result of the safety issues of carrying a cylinder of pure CO onboard the C-130, we will consider using either H_2 as the reducing agent or using a molybdenum mesh converter. Both approaches have been used previously (Bakwin et al., 1992; Fehsenfeld et al., 1987). A recent intercomparison in Tennessee (Williams et al., 1998) showed no inherent advantage for the gold or molybdenum converter in this type of environment. This is not to say that all converters performed equally well. In this intercomparison, two out of seven NOy converters (one gold, one molybdenum) showed lower NOy levels, at times, apparently due to loss of conversion efficiency. Thus, this study reinforces what many other studies have shown previously, that routine conversion efficiency tests are a prerequisite to making high quality NOy observations. A final decision on which converter will be made following discussions with NCAR aircraft personnel. If a molybdenum converter is chosen, it will use the smallest possible amount of metal mesh to avoid memory effects and a filter to ensure that molybdenum does not migrate downstream of the converter (Fehsenfeld et al., 1987).

In flight calibrations will be made using a NIST traceable ppmv standard of NO in N_2 which is diluted using calibrated mass flow controllers to a ppbv standard. In-flight zero air checks will also be made periodically with the highest quality zero air available. NOy conversion efficiency tests will be made in-flight with a calibrated HNO_3 source. NO and NOy will both be sampled from a rear facing Teflon inlet (e.g. Ridley et al., 1997). We will use a design similar to the one described by Ryerson (1999), which, based on the extensive laboratory and aircraft tests should transmit more than 90% of the HNO_3 present, even at ambient temperatures and humidities. This inlet design is fairly simple and should have even higher efficiencies for other NOy species. A rear facing inlet will exclude particles larger than about 1 um diameter. Size-segregated aerosol nitrate (and many other aerosol components) will be measured by several other investigators on the C-130. Because flow through both systems will be maintained continuously, inlet flow will not vary regardless of the instrument mode.

Other key measurements:

A number of other measurements will be measured as part of the standard aircraft observations or are being proposed for inclusion on the C-130. This includes O_3, CO, SO_2, CO_2, NMHCs, SO_2, H_2O vapor, size segregated aerosol chemistry, broad-band UV radiance, and, <u>possibly</u>, spectrally resolved actinic flux.

0-D photochemical modeling:

Previously, we have used the NCAR master mechanism (Madronich and Calvert, 1990) to interpret our NOx/O_3 observations (Herring et al., 1997). However we have just begun to use a photochemical model developed by Daniel Jacob and coworkers at Harvard University. This is in part due to the fact that one of Dr. Jacob's coworkers, Lyatt Jaegle, has accepted a faculty position at the University of Washington and we anticipate future collaboration. While Dr. Jaegle has no formal role in this project, she has agreed to offer some assistance in using the Harvard photochemical model. We will run the model in at least two different modes, steady state and Lagrangian. The steady state model runs will provide an estimate of NO_2 and OH from measured NO, O_3, CO, NMHCs, UV, etc. The Lagrangian model runs will be used in specific cases to help answer some of the question posed earlier (e.g. role of NO/NMHC ratios, temperature, role of photolysis rates, etc.).

The most difficult part of the modeling will be deriving photolysis rates. Using the UV radiometers, which will be onboard the C-130, it is straight-forward to derive $J(NO_2)$ photolysis frequencies (Madronich 1987). Obtaining values for $J(O^1D)$ is more difficult. This will be done by using a discrete-ordinate radiative transfer model in cooperation with S. Madronich at NCAR. This procedure is similar to what we have done in the past (Herring et al., 1997; Jaffe et al., 1998). The model calculated photolysis frequencies will be scaled to the measured UV irradiance, to account for aerosol and clouds effects. While it is plausible that the different spectral regions for $J(NO_2)$ and $J(O^1D)$ will result in large errors using this approach, a recent comparison of a variety of methods by Crawford et al. (1999) suggests that scaling both $J(NO_2)$ and $J(O^1D)$ to measured UV irradiances gives as good agreement to model calculated photolysis rates as any other approach. Alternatively, if spectrally resolved radiometric data are available, then we can use this to calculate the photolysis frequencies directly.

Data analysis strategies:

The data products we will generate include measured NO and NOy, and modeled OH and NO_2. NOx is calculated from the measured NO + the model calculated NO_2 and NO_Z is calculated from NOy-NOx. Combined with the other data onboard the C-130, this allows us the opportunity to examine the O_3 production using a number strategies. Initially, we should examine the basic relationship between a number of parameters (e.g. NOx, NOy, NOz, CO, O_3 and aerosol loading) to get an overview of the data. Then, we will segregate the data using a variety of strategies. For example, segregating by high and low aerosol loading, we can examine the CO-O_3 and CO-NOz relationships for evidence of changes in the ozone production efficiency (e.g. Parrish et al., 1991). We can segregate by aerosol chemistry to examine how different aerosols constituents may impact the photolysis rates and, therefore O_3 production (e.g. Dickerson et al., 1997). We can segregate the dataset by source region characteristics (NOx/NMHC emissions, temperature, etc.) to examine the influence of these variables on the O_3 production.

Finally, we expect that the NOx, NOy and OH values that we generate will prove to be extremely valuable (or essential) in meeting some of the broader ACE-Asia objectives and regional modeling. To our knowledge, no other research group has proposed nitrogen oxide measurements on the C-130 during ACE-Asia.

References

ACE-Asia [1999], Asian Pacific Regional Aerosol Characterization Experiment Project Prospectus, IGAC, December 1999. Available on-line at: http://saga.pmel.noaa.gov/aceasia/prospectus2000/

Akimoto H. and Narita H, Distribution of SO_2, NOx, and CO_2 Emissions from Fuel Combustion and Industrial Activities in Asia with $1^o x 1^o$ Resolution. Atm.Env. 28, 213-225, 1994.

Bakwin, P.S., S.C. Wofsey, S.M. Fan, and D.R. Fitzjarrald, Measurements of NOx and NOy concentrations and fluxes over Arctic tundra, *J. Geophys. Res., 97*, 16545-16557, 1992

Crawford J, Davis D, Chen G, Bradshaw J, Sandholm S, Kondo Y, Liu S, Browell E, Gregory G, Anderson B, Sachse G, Collins J, Barrick J, Blake D, Talbot R, Singh H. An assessment of ozone photochemistry in the extratropical western North Pacific: Impact of continental outflow during the late winter early spring. J. Geophys. Res. 102, 28,469-28,487, 1997.

Crawford J., Davis D., Chen G., Shetter R., Müller M., Barrick J. and Olson J. An assessment of cloud effects on photolysis rate coefficients: Comparison of experimental and theoretical values. J.Geophys.Res. 104, 5725-5734, 1999.

Chin, M., D.J. Jacob, J.W. Munger, D.D. Parrish, and B.G. Doddridge, Relationship of ozone and carbon monoxide over North America, *J. Geophys. Res., 99*, 14,565-14,573, 1994.

Denter FJ, Carmichael GR, Zhang Y, Lelieveld J, Crutzen PJ. Role of mineral aerosol as a reactive surface in the global troposphere. J. Geophys. Res. 101, 22,869-22,889, 1996.

Denter, F.J. and P.J. Crutzen, Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x, O_3, and OH, *J. Geophys. Res., 98,* 7149-7163, 1993.

Dickerson RR, Kondragunta S, Stenchikov G, Civerolo KL, Doddridge BG, Holben BN. The impact of aerosols on solar ultraviolet radiation and photochemical smog. Science 278, 827-830, 1997.

Drummond, J. W., A. Volz, and D. H. Ehhalt, An optimized chemiluminescence detector for tropospheric NO measurements, J. Atmos. Chem., 2, 287-306, 1985.

Duderstadt KA, Carroll MA, Sillman S, Wang T, Albercook GM, Feng L, Parrish DD, Holloway JS, Fehsenfeld FC, Blake DR, Blake NJ, Forbes G. Photochemical production and loss rates of ozone at Sable Island, Nova Scotia during the North Atlantic Regional Experiment (NARE) 1993 summer intensive. J. Geophys. Res. 103, 13531-13555, 1998.

Elliot S., Blake D.R., Duce R.A., Lai C.A., McCreary I., McNair L.A., Rowland F.S., Russell A.G., Streit G.E., and Turco R.P. Motorization of China implies changes in pacific air chemistry and primary production. *Geophys.Res.Letts.* 24, 2671-2674, 1997.

Fahey, D.W., C.S. Eubank, G. Hubler, and F.C. Fehsenfeld, Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NOy in the atmosphere, *J. Atmos. Chem., 3,* 435-468, 1985.

Fehsenfeld, F.C., R.R. Dickerson, G. Hubler, W.T. Luke, L.J. Nunnermacker, E.J. Williams, J.M. Roberts, J.G. Calvert, C.M. Curran, A.C. Delany, C.S. Eubank, D.W. Fahey, A. Fried, B.W. Gandrud, A.O. Langford, P.C. Murphy, R.B. Norton, K.E. Pickering, and B.A. Ridley, A ground-based intercomparison of NO, NOx, NOy measurement techniques, *J. Geophys. Res., 92,* 14,710-14,722, 1987.

Fehsenfeld FC, Daum P, Leaitch WR, Trainer M, Parrish DD, Hubler G. Transport and processing of O-3 and O-3 precursors over the North Atlantic: An overview of the

1993 North Atlantic Regional Experiment (NARE) summer intensive. J. Geophys. Res. 101, 28877-2889, 1996.

Finlayson-Pitts, B., F.E. Livingston, and H.N. Berko, Ozone depletion and bromine photochemistry at ground level in the Arctic spring, *Nature, 33,* 622-625, 1990.

Galloway J.N., Schlesinger W.H., Levy H. II., Michaels A. and Schnoor J.L. Nitrogen fixation: Anthropogenic enhancement-environmental response. Global Biogeochem. Cycles 9, 235-252, 1995.

He S and Carmichael GR. Sensitivity of photolysis rates and ozone production in the troposphere to aerosol properties. J. Geophys. Res., 104, 26307-26324, 1999.

Herring, J.A., D.A. Jaffe, H.J Beine, S. Madronich and D. R. Blake. High-Latitude Springtime Photochemistry. Part II. Sensitivity studies of Ozone Production, *J. Atmos. Chem.* 27, 155-178, 1997.

Hoell, J.M., D.D. Davis, S.C. Liu, R. Newell , H. Akimoto, R.J. McMeal, and R.J. Bendura, The Pacific Exploratory Mission-West, Phase B: February- March 1994, *J. Geophys. Res.*102, 28,223-28,239,1997.

Honrath, R.E. and D.A. Jaffe, The seasonal cycle of nitrogen oxides in the Arctic troposphere at Barrow, Alaska, *J. Geophys. Res.*, *97*, 20, 615-20, 630, 1992.

Jacob, D.J., J.A. Logan, G.M. Gardner, R.M. Yevich, C.M. Spivakovsky, S.C. Wofsy, S. Sillman, and M.J. Prather, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, *98*, 14,817-14,826, 1993.

Jacobson M.Z. Studying the effects of aerosols on vertical photolysis rate coefficient and temperature profiles over an urban airshed. J. Geophys. Res. 103, 10593-10604, 1998.

Jaffe D.A., Anderson T., Covert D., Kotchenruther R., Trost B., Danielson J., Simpson W., Berntsen T., Karlsdottir S. Blake D., Harris J., Carmichael G. and Uno I. Transport of Asian Air Pollution to North America. *Geophys. Res. Letts.* 26, 711-714, 1999.

Jaffe, D.A., Herring, J., and Madronich S., Impact of Large Solar Zenith Angles, Total Column Ozone and New O^1D Quantum Yields on Atmospheric Chemistry at High Latitudes. IGAC Activities Newsletter. 14, 8-10, 1998.

Jaffe, D.A., Mahura A., Kelley, J., Atkins J., Novelli P.C. and Merrill J. Impact of Asian Emissions on the Remote North Pacific Atmosphere: Interpretation of CO Data from Shemya, Guam, Midway and Mauna Loa. *J. Geophys. Res.* 102, 28,627-28,636, 1997.

Jaffe, D.A., R.E. Honrath, L. Zhang, H. Akimoto, A. Shimizu, H. Mukai, K. Murano, S. Hatakeyama and J. Merill, Measurments of NO, NO_y, CO and O_3 and estimation of the ozone production rate at Oki Island, Japan during PEM-West. *J. Geophys. Res.*, *101*, 2037-2048, 1996.

Kahl, J.D. “On the Prediction of Trajectory Model Error.” Atmospheric Environment, 30, 17, 2945-2957. 1996.

Kley, D. and M. McFarland, Chemiluminescence Detector for NO and NO_2, *Atmos. Tech., 12,* 63-69, 1980.

Liao H, Yung YL, Seinfeld JH. Effects of aerosols on tropospheric photolysis rates in clear and cloudy atmospheres. J. Geophys. Res. 104, 23697-23707, 1999.

Madronich, S., Intercomparison of NO_2 photodissociation and U.V. radiometer measurements, *Atmos. Environ.*, *21*, 569-578, 1987.

Madronich S., and Calvert J.G. Permutation Reactions of Organic Peroxy Radicals in the Troposphere. *J. Geophys. Res*. 95, 5697-5715, 1990.

Meagher JF, Cowling EB, Fehsenfeld FC, Parkhurst WJ. Ozone formation and transport in southeastern United States: Overview of the SOS Nashville Middle Tennessee Ozone Study. J. Geophys. Res. 103, 22213-22223, 1998.

Mozurkewich, M., and J.G. Calvert, Reaction probability of N2O5 on aqueous aerosols, *J. Geophys. Res., 93,* 15,889-15,896, 1988.

Nunnermacker LJ, Imre D, Daum PH, Kleinman L, Lee YN, Lee JH, Springston SR, Newman L, Weinstein-Lloyd J, Luke WT, Banta R, Alvarez R, Senff C, Sillman S, Holdren M, Keigley GW, Zhou X. Characterization of the Nashville urban plume on July 3 and July 18, 1995. J. Geophys. Res. 103, 28129-28148, 1998.

Parrish DD, Trainer M, Holloway JS, Yee JE, Warshawsky MS, Fehsenfeld FC, Forbes GL, Moody JL. Relationships between ozone and carbon monoxide at surface sites in the North Atlantic region. J. Geophys. Res. 103, 13357-13376, 1998.

Parrish, D.D., M. Trainer, M.P. Buhr, B.A. Watkins, and F.C. Fehsenfeld, Carbon monoxide concentrations and their relationship to concentrations of total reactive oxidized nitrogen at two rural U.S. sites, *J. Geophys. Res., 96*, 9309-9320, 1991

Parrish, D.D., J.S. Holloway, M. Trainer, P.C. Murphy, G.L. Forbes, F.C. Fehsenfeld, Export of North American ozone pollution to the North Atlantic Ocean, *Science, 259*, 1436-1439, 1993.

Parrish, D.D., M.P. Buhr, M. Trainer, R.B. Norton, J.P. Shimshock, F.C. Fehsenfeld, K.G. Anlauf, J.W. Bottenheim, Y.Z. Tang, H.A. Wiebe, J.M. Roberts, R.L. Tanner, L. Newman, V.C. Bowersox, K.J. Olszyna, E.M. Bailey, M.O. Rodgers, T. Wang, H. Berresheim, U.K. Roychowdhury and K.L. Demerjian, The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America, *J. Geophys. Res., 98*, 2927-2939, 1993.

Penkett SA, Volz-Thomas A, Parrish DD, Honrath RE, Fehsenfeld FC. Special section: North Atlantic Regional Experiment (NARE II) - Preface. J. Geophys. Res. 103, 13353-13355, 1998.

Prospero, J.M. and D.L. Savoie, Effect of continental sources of nitrate concentrations over the Pacific Ocean, *Nature, 339*, 687-689, 1989.

Ridley, B. A. ; Atlas, E. L. ; Walega, J. G. ; Kok, G. L. ; Staffelback, T. A. ; Greenberg, J. P. ; Grahek, F. E. ; Hess, P.G. ; Montzka, D. D. 1997. Aircraft measurements made during the spring maximum of ozone over Hawaii: Peroxides, CO, O_3, NOy, condensation nuclei, selected hydrocarbons, halocarbons, and alkyl nitrates between 0.5 and 9 km altitude. *J. Geophys. Res* 102, 18935-18961, 1997.

Ridley, B.A. and F.E. Grahek, A small low flow, high sensitivity reaction vessel for NO chemiluminescence detectors, *J. Atm.and Oceanic Tech., 7*, 307-311, 1990.

Ridley, B.A., M.A. Carroll, G.L. Gregory, and G.W. Sachse, NO and NO2 in the troposphere: Technique and measurements in regions of a folded tropopause, *J. Geophys. Res*., *93*, 15,813-15,830, 1988.

Ryerson TB, Huey LG, Knapp K, Neuman JA, Parrish DD, Sueper DT, Fehsenfeld FC. Design and initial characterization of an inlet for gas-phase NOy measurements from aircraft. J. Geophys. Res. 104, 5483-5492, 1999.

Sillman S. The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments. Atmos. Env. 33, 1821-1845, 1999.

Sillman S and Samson F.J. Impact of temperature on oxidant photochemistry in uran, polluted, rural and remote environments. J. Geophys. Res. 100, 11497-11508, 1995.

Stohl A. Computation, accuracy and applications of trajectories- A review and bibliography. Atmos. Env. 32, 947-966, 1998.

Streets DG, Carmichael GR, Amann M, Arndt RL (1999) Energy consumption and acid deposition in northeast Asia. *Ambio* 28, 135-143.

Talbot R.W. et al., Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during February-March 1994: Results from PEM-West B. *J. Geophys. Res.* 102, 28,255-28,274, 1997.

Van Aardeen, G. Carmichael, D. Streets, H. Levy, and L. Hordijk, Anthroprogenic NOx emissions in Asia in the period 1990-2020 (1999). Atmos. Env. 33, 633-646.

Williams, E.J., Baumann, K., Roberts, J.M., Bertman, S.B., Norton, R.B., Fehsenfeld, F.C., Springston, S.R., nunnermacker, L.J., Newman, L., Olszyna, K., Meagher, J., Hatsell, B., Edgerton, E., Pearson, J.R., Rodgers, M.O. Intercomparison of Ground-Based NOy Measurement Techniques. J. Geophys. Research, 103, 22,261-22,280, 1998.